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ELECTROCHEMISTRY IN LIQUID CRYSTALS:

ORIENTATIONAL EFFECTS IN ELECTROCHEMICAL PROCESSES

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Abstract:

The electrochemical characterization of the room temperature nematic phases MBBA (p-methoxybenzilidene p-butyl aniline), MBAB (methoxy-butyl azoxybenzene) and K-15 (4-pentyl-4' cyano-biphenyl) has been performed in acetonitrile as well as in the neat phases and it is found that they all possess a wide range of potentials over which electrochemical experiments can be carried out. MBBA and MBAB exhibit large ohmic drops making experimentation difficult. K-15, on the other hand, proved to be very well behaved. A number of model redox couples were investigated in K-15 and it is found that the electrochemical response can be significantly different from that observed in conventional solvents such as acetonitrile. These differences can be ascribed to the formation of ion aggregates as well as to differences in diffusion coefficients. We also present some preliminary findings on the effect of orientation on the observed electrochemical response of TCNQ (tetracyanoquinodimethane), ferrocene and TCNE (tetracyanoethylene).

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Introduction:

One of the central goals of electrochemical research is to control the reactivity of substrate molecules at the surface of an electrode.

In the present context we are trying to control electrochemical reactivity through solute/solvent interactions. Specifically, we are interested in ascertaining how the electrochemical behavior and transport properties of redox systems are altered when electrochemical experiments are carried out in highly ordered solvent systems. In such an environment a redox species can be oriented in a particular fashion, relative to the electrode surface, and this allows for the study of the effects of orientation on redox potentials, rates of electron transfer as well as transport rates. We are approaching this by making use of liquid crystals as solvents in which to perform electrochemical experiments.

Liquid crystals (l.c.) encompass a variety of chemical species whose most prominent feature is that they exhibit more than a single transition in going from solid to isotropic liquid. (1-3) It is these intermediate phases that are known as mesophases or liquid crystals. Liquid crystals are generally catalogued as being either thermotropic or lyotropic. Thermotropic liquid crystals are those in which transitions are effected by changes in temperature. These materials are further subdivided into nematic, cholesteric and smectic. The nematic phase is characterized by having long range orientational order with a principal axis in a fixed direction. For these phases, the temperature at which the nematic phase is converted into an isotropic liquid is known as the nematic/isotropic (n/i) transition temperature. There are significant changes in physicochemical properties that accompany such a transition. For example, nematic phases scatter light very strongly whereas the isotropic phases are clear. In addition, there are significant changes in viscosity. The cholesteric phase is similar to the nematic,
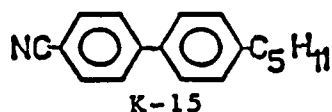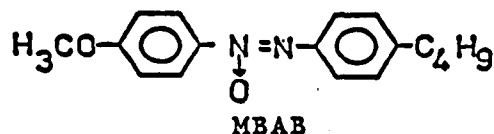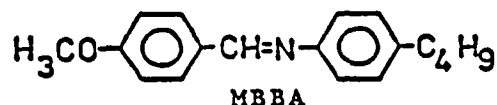
but in this case the principal axis follows a helical course so that cholesteric phases exhibit optical activity. The smectic phases are characterized by having one degree of translational ordering resulting in layered structures which are much more viscous than either the nematic or cholesteric phases.

Another salient feature of liquid crystals is that they can be oriented in parallel or perpendicular fashion relative to a surface and that this orientation can be accomplished in a variety of ways including electric (4) or magnetic fields (5), addition of surfactants (6), evaporation of inorganic films onto a surface (7) and others. Furthermore, it is known that interacting solutes dissolved in oriented liquid crystals will themselves be oriented by the liquid crystalline phase.(8-12)

As far as electrochemical studies of liquid crystals is concerned, most have been related to the use of liquid crystals for display devices. Of special interest in this respect is a phenomenon known as dynamic scattering. This is a conduction-induced fluid flow which takes place when a nematic phase is subjected to an applied voltage. In investigating dynamic scattering, some mesophases have been electrochemically characterized as to accessible potential limits.(13-17) There have also been studies where the conductance of liquid-crystal electrolyte systems has been investigated.(18,19) In recent studies, Margerum and Barret (20,21) used electroactive dopants in nematic phases and found that these reduce the potential required for the onset of dynamic scattering. Herino and coworkers have also reported some voltammetric studies in mesophases.(22-25)

We describe a series of studies on the electrochemical characterization of three room temperature nematic phases: MBBA (p-methoxybenzilidene p-butyl aniline), MBAB (methoxy-butyl azoxybenzene) and K-15 (4-pentyl-4'cyano-biphenyl) (see

structures below). MBBA was investigated because it is one of the best

$$H_3CO-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-C_4H_9$$

MBBA

$$H_3CO-\langle\bigcirc\rangle-\underset{\overset{\downarrow}{O}}{N}=N-\langle\bigcirc\rangle-C_4H_9$$

MBAB

$$NC-\langle\bigcirc\rangle-\langle\bigcirc\rangle-C_5H_{11}$$

K-15

characterized liquid crystals, MBAB for its very broad nematic temperature range (up to 75° C) and K-15 because of its stability, relatively high dielectric constant and because preliminary studies by Gosse (14) on the heptyl analog indicated a broad range of accessible potentials.

In addition, we present electrochemical studies on a number of redox species in these liquid crystalline matrices including some preliminary results on the effects of orientation on the electrochemical behavior.

Experimental:

A. Reagents:

MBBA (Frinton Laboratories) and MBAB (E.M. Chemicals) were vacuum distilled. K-15 was obtained from Atomergic Chemetals and E.M. Chemicals. We also prepared this material by a modified version of the procedures given by Gray and coworkers (26) and Oh (27). Acetonitrile (Burdick and Jackson Distilled in Glass) was dried over 4A molecular sieves.

Tetra n-butyl ammonium perchlorate (TBAP, G. F. Smith) and tetra n-butyl ammonium tetrafluoroborate (TBAF, Southwestern Analytical) were recrystallized

three times from ethyl acetate and dried in vacuo at 70°C for 72 hrs.
Tetrahexyl ammonium perchlorate was prepared by mixing aqueous solutions of
tetrahexyl ammonium bromide and perchloric acid. The precipitated salt was washed
with water, dried and recrystallized thrice from ethyl acetate. Tetrabutyl
ammonium tetraphenyl borate was prepared by mixing aqueous solutions of tetra
n-butyl ammonium bromide and sodium tetraphenyl borate. The precipitate was washed
with water, dried and recrystallized from acetone/ether. Dicyclohexyl
18-crown-6/KBF$_4$ (18C-6/KBF$_4$), 15-crown-5/sodium tetraphenyl borate (15C-5/Naϕ_4B)
and cryptofix-2-2-2/KBF$_4$ (K*/BF$_4$) were prepared by mixing stoichiometric
methanol solutions of the salt and the ligand. The solutions were stirred for 1hr
and the methanol removed under vacuum. The resulting white solids were washed with
water and ether and dried in vacuum.

All of the redox active components investigated were purified by either
recrystallization or by sublimation.

B. Instrumentation:

Electrochemical experiments were performed with P.A.R. models 173
Potentiostat, 179 Digital Coulometer and 175 Universal Programmer or with a locally
built potentiostat and signal generator. Data were recorded on either Soltec or
Hewlett Packard X-Y recoders. For experiments in acetonitrile, conventional three
compartment cells, separated by medium porosity frits, were employed.

For experiments with the neat liquid crystalline phases, a single compartment
cell was constructed from a $29/42 joint. The male part was provided with 4 $10/30
joints through which the three electrodes were connected and where the fourth
connection was used to evacuate the cell. The bottom part of the joint was cut and
ground flat and a pyrex flat was attached, to make the cell bottom, using paraffin
and epoxy. The thickness of the l.c. layer was typically 3 mm. Alternatively,

cells were constructed from 3 dram pyrex vials whose bottoms were cut and polished flat. The cell bottoms consisted of micrscope slides which were attached as described above for the pyrex flats. In all cases a platinum working electrode (shrouded in glass) and a platinum counter electrode were used.

Potentials in acetonitrile are referenced to an aqueous sodium saturated calomel electrode (SSCE). In the liquid crystals, either a silver quasireference electrode or an Ag/Ag^+ reference electrode (10 mM $AgBF_4$ dissolved in the liquid crystal in contact with a silver wire) were used.

D. Orienting Materials:

The pyrex flats and glass slides used as cell bottoms were treated with either ACM-72 or Surfine 150 (both from Atomergic Chemetals) according to the manufacturers procedure. These materials produce surfaces that will orient the liquid crystal parallel and perpendicular to the surface, respectively. Orientation of the liquid crystalline layers was confirmed by the use of an optical microscope with crossed polarizers. To prevent contamination, the pyrex flats and glass slides were used only once.

Results:

A. Electrochemical Characterization of Liquid Crystalline Phases:

In order to assess the potential limits within which the l.c. phases could be employed in electrochemical studies, their electrochemical characterization in acetonitrile/TBAP was performed.

MBBA was investigated first since there were already some studies on its electrochemical characterization. Similar to the results reported by Bard and coworkers (17), we find that MBBA has two irreversible oxidation processes at E_p values of +1.43 and +2.05 volts vs SSCE respectively. (The latter, however,

appears to be a composite of at least two waves since there is a shoulder present.) We also observe an irreversible reduction with an E_p value of -2.10 V vs. SSCE, again in good agreement with previous reports.

The electrochemical response of MBAB in acetonitrile/TBAP exhibits two well defined irreversible oxidation waves at E_p values of +1.59 and 1.75 V vs. SSCE respectively, as well as two additional waves at +1.95 and +2.18 V. MBAB has a single reduction wave with an E_p value of -1.58 V. In this case, there is a current peak on the reverse sweep, indicating some stability of the product. At sweep rates above 20V/s the wave appeared to be chemically reversible and an $E^{o'}$ value of -1.53 V was obtained. A sweep rate study of this wave coupled with controlled potential electrolysis seems to indicate an ece type mechanism, however, no further studies were performed.

K-15 had two irreversible oxidations (Figure 1A) at E_p values of +2.01 and +2.41 V. vs SSCE as well as one reversible reduction wave with a formal potential of -2.09 V vs. SSCE. This latter process is likely due to the generation of the radical anion. (e.g. analogous to benzonitrile and related materials) Comparison of the peak currents for the reductive and oxidative processes seems to indicate that the latter involve multielectronic transfers.

Using these measured potentials as a guide, the operating range of potentials for the different materials were operationally defined to be about 150 mv positive and negative of the first reductive and oxidative processes, respectively. This represents a lower limit, since in the neat phases the ion radicals generated are expected to be much more poorly solvated and as such the range of accessible potentials will likely be extended over the values mentioned.

B. Supporting Electrolyte Studies:

In order to be able to employ these l.c. phases as electrochemical solvents, the appropriate supporting electrolytes had to be identified. This presented some difficulties since these materials typically have small dielectric constants, therefore, even if dissolved, the degree of dissociation of an electrolyte would be expected to be small. In addition, we did not know in what way(s) the presence of a supporting electrolyte would affect the other properties of the l.c. phases. A number of supporting electrolytes were screened including traditional ones such as TBAP and TBAF as well as more esoteric systems such as KBF_4/Kriptofix-2,2,2 (K^*BF_4) and others (see experimental section). The studies were performed by adding excess supporting electrolyte and warming the l.c. past its nematic/isotropic (n/i) temperature in order to enhance dissolution, and stirring for 1 hr. The l.c. was allowed to cool and the undissolved electrolyte was filtered off. A cyclic voltammogram at low sweep rate (typically 20 mV/s) was then performed on the l.c. with the dissolved electrolyte. From the properties of the voltammogram obtained, a qualitative judgement could be made as to the utility of the given supporting electrolyte. (The criterion employed was the presence of flat voltammetric charging currents such as those shown in Figure 2.) From these studies, it was determined that for both MBBA and MBAB the best system was K^*BF_4 whereas for K-15, TBAF was not only soluble, but in addition seemed to dissociate to a significant extent. This is consistent with the larger dielectric constant of K-15 (ca. 16). In adddition, it was found that, for K-15, when the concentration of the supporting electrolyte was above 80mM, there seemed to be a significant disruption of the l.c. phase as evidenced by the fact that the l.c. turned clear (indicating the transition from the nematic to the isotropic phase). Due to this, electrolyte concentrations were kept below these values— typically at 35mM.

Figures 2 A-C show cyclic voltammograms for the different l.c. phases with the appropriate supporting electrolytes. From the voltammograms it was determined that the range of accessible potentials was somewhat broader than we had originally estimated, consistent with the arguments presented previously concerning the solvating ability of these phases. A decrease in the solution resistance was noticed as the temperature was raised (especially at temperatures above the n/i transition) consistent with a higher degree of dissociation of the supporting electrolyte.

C. Electrochemical Studies in Liquid Crystals:

Having identified suitable supporting electrolytes for the various l.c. phases, we attempted the electrochemical characterization of a number of electrochemically well behaved redox systems. In general we found that the very high ohmic resistance of both MBBA and MBAB made electrochemical studies difficult. The observed voltammetric responses were typically very broad, and in many instances a response was obtained only when the solvents were present in the isotropic phase.

Electrochemical studies in pentylcyano biphenyl (K-15):

Contrary to both MBBA and MBAB, K-15 was a well behaved solvent for electrochemical studies both in the liquid crystalline and isotropic forms, allowing the investigation of a wide range of electroactive materials. In addition, we were able to perform some studies on the effect of orientation on the observed electrochemical response. We begin by considering the redox characterization of the different systems and afterwards we will focus on orientational effects.

Although K-15 was a well behaved solvent for electrochemical studies, the fact that we had to keep the concentration of supporting electrolyte low (vide-supra) meant that large ohmic drops were typically encountered. Nevertheless, a number of materials gave well defined responses including decylviologen, dodecylviologen, ferrocene, $Ru(bpy)_3^{+2}$, $Fe(bpy)_3^{+2}$, TCNQ, TCNE, tetramethylbenzidine (TMB) and chloranil.

In the viologen group both the decyl and dodecyl derivatives gave well behaved responses whereas methyl viologen did not give a measurable response. (Figure 3A-B) This might point towards a more favorable solute/solvent interaction with increasing length of the hydrocarbon chain as well as enhanced solubility. There was also a very dramatic supporting electrolyte concentration effect. Specifically, when the concentration of supporting electrolyte was about 0.1M, a very well defined electrochemical response was obtained, although the ΔE_p value was still over 150 mV (Figure 3C). In addition, the l.c crystal turned clear even though the temperature was well below the n/i transition temperature, an indication that an isotropic and not a liquid crystalline phase was present. The peak current was also enhanced as compared to values obtained at say 35mM supporting electrolyte concentration reflecting the significant change in viscosity that accompanies the transition. Peak currents similar to those observed at 0.1M concentration of supporting electrolyte could be obtained at a concentration of 0.04M if the temperature of the medium was adjusted to be above the n/i transition (47°C), again consistent with the previous results. A sweep rate dependence study (for the dodecyl derivative) showed that the the formal potential for reduction remained invariant and a plot of peak current vs. square root of the sweep rate was linear (r = 0.998) indicating a diffusion controlled process. Analogous results were obtained for the decylviologen, $Ru(bpy)_3^{+2}$ and $Fe(bpy)_3^{+2}$.

Ferrocene, TCNE, TCNQ and TMB were among the best behaved redox systems investigated in these studies. Very well developed voltammograms could be obtained when the K-15 was present in either liquid crystalline or isotropic form. As with the other systems, the peak current increased and the ΔE_p values decreased at temperatures above the n/i transition temperature. The formal potentials were independent of sweep rate and the dependence of the peak current on the square root of the sweep rate indicated that the processes were diffusion controlled. These systems were investigated with regards to possible specific solvent and orientational effects and as such will be discussed in more detail below.

D. Specific Solvent Effects:

The fact that liquid crystals are highly ordered systems and oriented layers can in turn orient substrate molecules dissolved in them raised the tantalizing question of whether the electrochemical response of a given reactant could be altered by orienting it relative to an electrode surface. The highly anisotropic properties of liquid crystals (e.g. viscosity and dielectric constants) could also affect transport rates and kinetics of electron transfer.

To determine if there are orientational or specific solvent effects, many variables need to be considered. Of particular importance are the mode of alignment employed for the liquid crystalline matrix, the propagation distance of such alignment and the types of molecules used to ascertain if such an effect is indeed present.

In addition, there could be (and more than likely there are) solvent/solute interactions that are not related to orientational effects and allowance must be made to account for these.

Finally, since the experimental observables are potential and current, one

must be certain that these will be sufficiently stable during the course of the experiment.

In order to mitigate the large ohmic drops that were typical of these systems, we used small area platinum electrodes (350 micrometer diameter) which gave well behaved responses and easily measured currents with tolerable ohmic drops.

Since the accurate and reproducible measurement of potentials was deemed critical, close attention was given to the design of an appropriate reference electrode and after examining a wide range of materials we concluded that the most reliable measurements were obtained by using the Ag^+/Ag couple. Specifically, we found that a silver wire in contact with a solution of the liquid crystal with 10mM $AgBF_4$ gave very reproducible results and this reference electrode was used in subsequent studies. In order to test the stability of this reference electrode we examined the electrochemical response of ferrocene in an unoriented layer of K-15/TBAF. We found that the formal potential (taken as $(Ep_c + Ep_a)/2$) varied by no more than 8 mV during the course of 24 hrs. We also used the measured values of the formal potentials of ferrocene in the liquid crystal ($E^{0\prime}$ = +0.09 V vs. Ag^+/Ag) and in acetonitrile ($E^{0\prime}$ ≈ +0.438 V vs. SSCE) to provide a means of relating the measured potentials in the liquid crystal with those measured in acetonitrile. This analysis places the Ag^+/Ag potential in K-15 at −0.348 V vs. SSCE. Although this approach is widely used, its validity could be argued. Nontheless, it provides a means for comparing redox potentials in both solvents. Variations in the measured peak currents were about 10% during the same time interval if the solutions were kept under nitrogen and away from direct light. These results pointed to the fact that reproducible potential and current values could be obtained under these conditions.

1. TCNQ:

The electrochemical response of TCNQ in K-15/TBAF was characterized by two well developed voltammetric waves (Figure 4) at $E^{o\prime}$ values of -0.195 and -0.950 V vs. Ag^+/Ag respectively. Although on a cathodic going sweep the waves appeared diffusional (and in fact a plot of i_p vs $(v)^{1/2}$ was linear) the anodic counterpart of the wave centered at -0.950 V was much sharper, typical of processes involving adsorption. Upon warming past the n/i temperature (to 42^oC) the shape of this wave changed to that typical of a diffusion controlled process (Figure 4) and upon cooling back to a liquid crystalline state, it reverted back to the adsorptive-like shape. We ascribe this to adsorption or precipitation of the dianion of TCNQ on the electrode surface. However, holding the potential of the electrode past the second reduction wave for a period of five minutes did not cause a significant enhancement of the peak current of this wave, indicating that the material does not accumulate on the electrode surface.

More dramatic were the effects on the formal potentials for the processes as well as the $\Delta E^{o\prime}$ values. In acetonitrile/TBAP, TCNQ exhibits two reversible one electron reductions at $E^{o\prime}$ values of $+0.240$ and -0.302 V vs SSCE. If we apply the correction factor derived form the measurements on ferrocene we obtain values of $+0.153$ and -0.602 V vs. SSCE for TCNQ in K-15. Not only are these values significantly shifted from the values observed in acetonitrile, but the $E^{o\prime}$ value increases from 542 mv in acetonitrile to 755 mv in K-15, indicative of a very strong solvent effect in these processes, especially for the second reduction. Such shifts could imply that the liquid crystal has very different affinities for the TCNQ, its radical anion or dianion. However, the direction of the shifts would indicate that the liquid crystal interacts more strongly with the TCNQ than with the ion radical or dianion. Although we have no evidence to discount

this, we believe that the opposite (that is the liquid crystal interacting more strongly with the dianion and ion radical than with the TCNQ) would be more probable. It should also be mentioned that the voltammetric response of TCNQ in benzonitrile/TBAF was essentially identical to that in acetonitrile indicating that the benzonitrile-like part of K-15 is not responsible for the observed effect. An alternative explanation could be formulated in terms of large differences in the diffusion coefficients for the different species.(28) In this framework, the dianion would have a smaller diffusion coefficient than the ion radical which would in turn have a smaller diffusion coefficient than the parent TCNQ. This is quite plausible if we consider that the ion radical and dianions are likely to be strongly ion-paired and as such would exhibit much smaller diffusion coefficients. This would be in accordance with studies of Herino and co-workers (24) who reported large differences for the diffusion coefficients (in liquid crystalline phases) of tetramethylp-phenylenediamine (TMPD) and its ion radical. These differences were ascribed to strong ion-pairing and this was confirmed via conductometric experiments.

In order to test for the effect of ion-association (ion pairs or higher aggregates) voltammetric studies of TCNQ in THF with 35mM TBAF as electrolyte were performed. Given the low dielectric constant of THF, the presence of ion association should be quite apparent, and in fact, the voltammetric response for TCNQ under these conditions shows that the $\Delta E^{o\prime}$ value (650 mV) is close to that observed in K-15. However, the fact that in K-15 the $\Delta E^{o\prime}$ value is still significantly higher, points to the presence of an additional effect that we have not yet identified.

We have also performed analogous studies on chloranil in K-15/TBAF and although the electrochemical response observed is not as well defined as for TCNQ,

the $E^{o\prime}$ values in acetonitrile and K-15 remain essentially the same. (There is, however, a small shift in the $E^{o\prime}$ values to somewhat more negative potentials (ca. 100 mV).) Since these redox processes also involve the generation of an ion radical and a dianion we had anticipated that ion pairing would also play a prominent role and thus lead to large variations in the diffusion coefficients. This in turn would give rise to the shifts observed for TCNQ. The fact that smaller shifts were observed seems to indicate that there are other effects involved in the case of TCNQ, perhaps the formation of a charge transfer complex. In fact TCNQ in K-15 has an orange color whereas in acetonitrile it is yellow. This points to the presence of either a charge transfer complex or a very strong solvatochromatic shift; and we are currently undertaking a spectral study of this effect.

TMB:

A cyclic voltammogram of TMB in K-15/TBAF (figure 5) exhibits two well developed oxidation waves at E_p values of +0.30 and +0.575 V vs Ag+/Ag, whereas a reductive sweep shows only a single reduction wave at an E_p value of -0.245 V. This latter wave has an adsorptive shape and the area under it is much larger than either of the anodic waves but comparable to the sum of the areas of the two anodic processes. If a cathodic sweep is initiated after the first oxidation wave, no reduction current is observed. The shape of the voltammetric response remained unchanged upon warming the solution to 42°C (past the n/i transition) although the waves were shifted on the potential scale, probably reflecting a decrease in the ohmic drop of the solution. This response is to be contrasted with that of TMB in acetonitrile/TBAF where two reversible one electron redox process are observed at $E^{o\prime}$ values of +0.470 and +0.650 V vs SSCE.

The electrochemical response of TMB in K-15 proved to be very sensitive to the addition of very small amounts of acetonitrile/TBAF. Such addition caused the K-15 layer to become transparent, indicating that the liquid crystallinity had been lost; and the resulting voltammetric response was very similar to that observed in acetonitrile/TBAF.

We had suspected that the high viscosity of the K-15 might be responsible (at least in part) for the observed behavior. In order to ascertain this, we performed cyclic voltmmetric experiments of TMB in dimethylsulfoxide (DMSO) whose viscosity was adjusted by the addition of sucrose according to the procedure of Bard and coworkers.(29) The shape of the electrochemical response of TMB remained essentially unchanged in solutions whose viscosities ranged from 5 to 50 cP. The viscosity of K-15 at 22°C can be as high as 39 cP (measured perpendicular to the director) (30,31) and since in the previous experiments we did not see any dramatic change in the waveshape in a solvent of comparable viscosity, we do not believe that the viscosity of K-15 is responsible for the observed response. This is further confirmed by the fact that warming the K-15 soluion past the n/i temperature did not significantly alter the wave shape although the viscosity at this temperature is of the order of 18 cP. We believe that the anodic processes correspond to the oxidation of TMB to the cation radical and dication and that the cathodic wave represents the reduction of the dication to the neutral TMB in a two electron process. The fact that the reduction waves for TMB merge into a single wave whose potential is shifted negative of the corresponding processes for TMB suggests the presence of a significant barrier to electron transfer. This could be due to the formation of a tight ion triplet with a high overpotential for reduction. In addition, the direction of the shift is consistent with a stabilization of the dication of TMB by the K-15.

In order to test for the formation of ion aggregates, we performed voltammetric measuremenmts in THF/TBAF(35mM). Under these conditions the waveshape of TMB is essentially identical to that obtained in K-15. (Figure 5 inset) Given the low dielectric constant of THF and the fact that no significant interaction of the radical cation and dication with THF would be expected, we are inclined to ascribe the observed behavior to the formation of very tight ion aggregates (pairs and triplets). Furthermore, the addition of acetonitrile/TBAF (35mM) changed the voltammetric response to that observed in acetonitrile/TBAF. Thus, it is clear that the response of TMB in K-15 is dominated by ion aggregation effects.

Orientational Effects:

As mentioned previously l.c. can be oriented by the use of electric and magnetic fields as well as by the modification of surfaces with surfactants or other materials. Since the use of electric or magnetic fields could severely interfere with electrochemical measurements, we decided to employ surfactants for orienting the l.c. phases. Thus we chose Surfine 150 and ACM-72 (see experimental section) as materials to obtain a homogeneous (parallel to the surface) and a homeotropic (perpendicular to the surface) alignment, respectively. In terms of propagation of the alignment, this can vary widely depending on specific systems, but distances as large as 1 cm have been reported. (32,33) We tried to minimize the distance between the orienting layer (the cell bottom) and the working electrode by having the electrode rest on it. Such an arrangement is estimated to give an effective distance of about 20 to 50 microns between the electrode and the cell bottom.

When considering orientational effects in the present context, one must

distinguish between the effects due to the anisotropy in properties of the liquid crystal (for example dielectric constant and viscosity) from other specific solute/solvent interactions. We initially focused on viscosity effects since the temperature dependence of the viscosity of K-15 had been previously determined (31) and we could estimate an effective viscosity from an electrochemically determined diffusion coefficient and the Stokes-Einstein relation. The initial measurements were on ferrocene and TCNQ in K-15. The K-15 was oriented parallel to the surface by either the use of ACM-72 or by simply using a clean polished glass slide since this is also known to give rise to this orientation for K-15. Given the fact that the viscosities in the parallel and perpendicular directions are quite different from each other and from that of the isotropic phase, the measurement of diffusion coefficients appeared to be a very attractive way of determining the orientation of the liquid crystalline layer and the interaction of the solute with it. Specifically this could be ascertained from the peak currents for the different orientations as well as for the isotropic phase. Since the viscosity of the isotropic phase was known, we could derive a value for the viscosity of the liquid crystalline phase and from this infer the orientation.

For example, for ferrocene in K-15 oriented parallel to the surface (at 25°C) or present as an isotropic phase (at 42°C) we find that the diffusion coefficients are 2.7 and 5.8 $\times 10^{-8}$ cm^2/s, respectively. Taking the value of the viscosity of K-15 at 42°C as 18 cP (31) and comparing the ratio of the diffusion coefficients under both conditions, we obtain an effective viscosity of 36.6 cP for the K-15 in the liquid crystalline form. This is in good agreement with the reported value of 39cP (31) for the viscosity of K-15 perpendicular to the director (at 25°C). (The fact that the K-15 is oriented parallel to the electrode surface implies that the appropriate viscosity will be that which is perpendicular to the director as

found.) If the liquid crystal had been oriented perpendicular to the surface, the viscosity would have been expected to be close to 28cP which is the value measured parallel to the director.

In the case of TCNQ we find similar results with the diffusion coefficients being 4.0 and 8.6 $x10^{-8}cm^2/s$ for the liquid crystal (at $25^{\circ}C$) oriented parallel to the electrode surface and as an isotropic phase (at $42^{\circ}C$) respectively. We can estimate that the effect of temperature alone will account for no more than a 10% difference in the diffusion coefficients. (This would be the difference in diffusion coefficients if the experiments could be performed at two temperatures in solvents of identical viscosity.)

It should be mentioned that there was some scatter in the values of the diffusion coefficients, however, the relative magnitudes were reasonably reproducible. (The scatter is due in part to uncertainties in the weighing of the electroactive material (typically a few micrograms) since due to the cost of the liquid crystal we typically prepared 1ml portions for study.) In addition, we believe that the presence of an electrolyte in the liquid crystal will affect the viscosity of the medium, however, as a first approximation we have chosen to neglect this effect. Finally, we would also like to make some remarks (based on some preliminary results) concerning the formal potential for the reduction of TCNE under different orientations. Although there was some scatter in the data, there appears to be a trend where the formal potential for reduction in the homogeneous orientation is positive of that in the perpendicular orientation. The use of ferrocene as an internal standard, however, allowed the reliable measurement of differences in $E^{\circ}{}'$. This effect, (about 20 mV beyond experimental error) could be rationalized in terms of stabilization of reactant or product or in terms of orbital overlap between the reactant and the electrode. These are only

tentative interpretations and at this time we cannot unambiguously identify the phenomena associated with these observed shifts.

We are presently involved in a very systematic study of the variations of peak currents and formal potentials for various redox couples under different orientations and from these studies we hope to be able to firmly establish the nature of these observed effects. We are also currrently addressing the effect of the electric field at the working electrode on the propagation distance of the nematic, which may elucidate the proposed orientation effects for the TCNE/K-15 system.

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Figure Legends:

Figure 1. Cyclic Voltammogram at 200 mV/s for a 1mM solution of K-15 in acetonitrile/TBAP (A). Sweep between 0.0 and +2.5 V. (B). Sweep between 0.0 and -2.5 V.

Figure 2. Cyclic voltammograms for the liquid crystals as solvents containing the appropriate supporting electrolyte.

A. MBBA/K*BF_4,20 mV/s S=0.2 μA

B. MBAB/K*BF_4; 20 mV/s S=0.2 μA

C. K-15/TBAF; 20 mV/s S=0.2 μA

Figure 3. Cyclic voltammograms at 10mV/s for long chain viologens in K-15 with 35mM TBAF.

A. 3.5 mM decyl viologen; S=50nA

B. 2.2mM dodecyl viologen; S=20nA

C. 3.25 mM dodecyl viologen with 0.1M TBAF S=50nA

Figure 4. Cyclic voltammograms for 2.54 mM TCNQ in K-15 with 35mM TBAF.
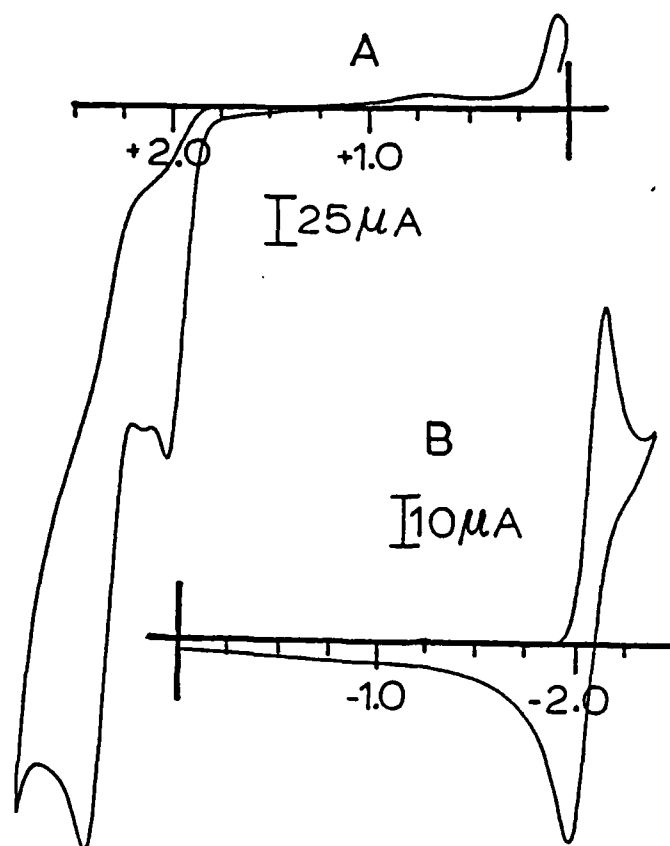
A. at 22°C sweep rate is 10mV/s S=10nA

B. at 42°C (isotropic) at 20mV/s S=50nA

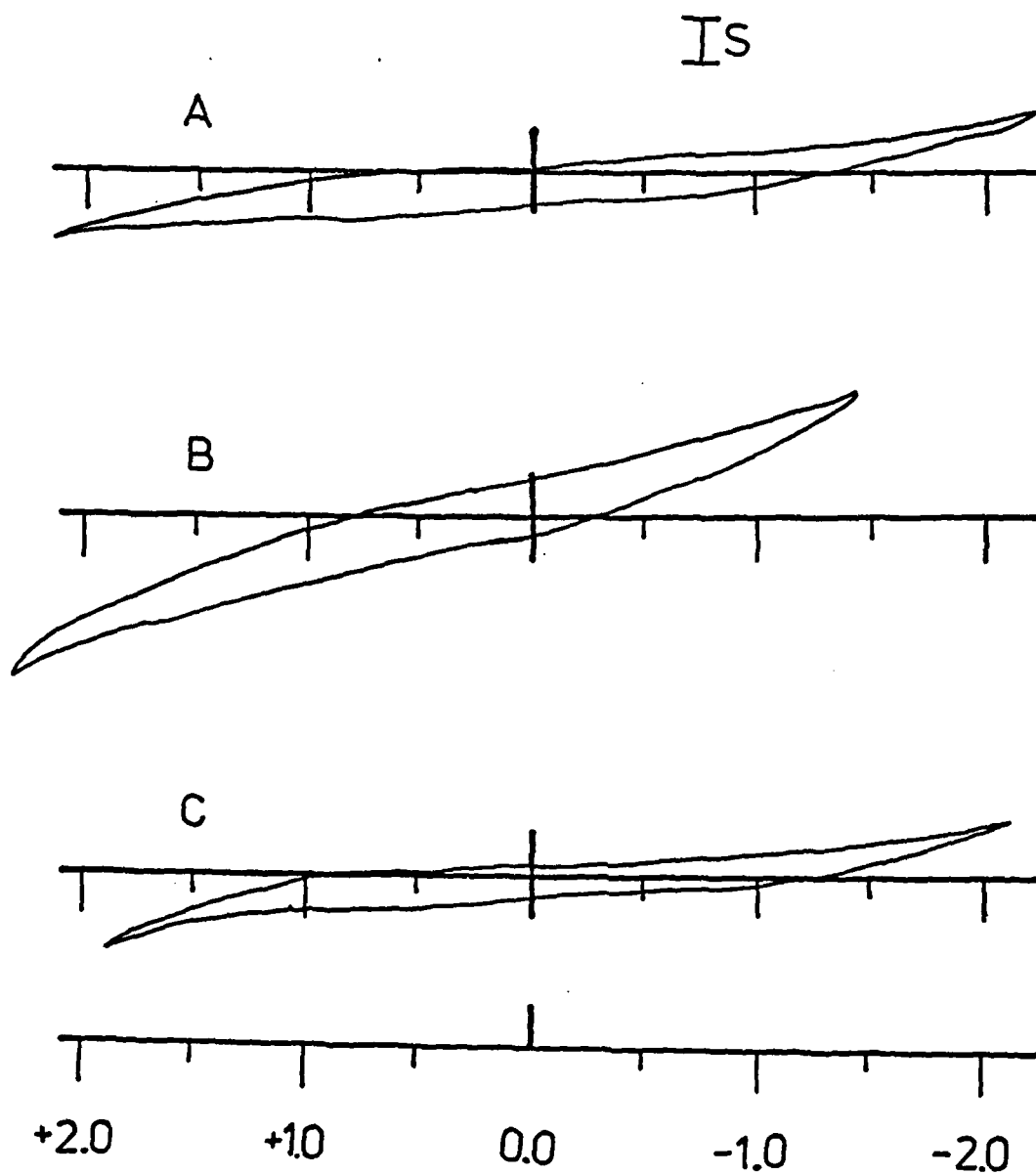Figure 5. Cyclic voltammograms at 10mV/s for 2.1mM TMB in K-15 with 35 mM TBAF.

A. at 22°C

b. at 42°C (isotropic)

(inset): Cyclic voltammogram at 50mV/s for 1mM TMB in THF with 35 mM TBAF

A

+2.0   +1.0

$\underline{\mathrm{I}}25\mu A$

B

$\underline{\mathrm{I}}10\mu A$

-1.0   -2.0

E vs.SSCE

Figure 1

Is

A

B

C

+2.0   +1.0   0.0   -1.0   -2.0

E vs Ag°

Figure 2

A

B

Is

C

E vs Ag°

Figure 3

S

A

−0.5   −1.0   −1.5

B

E vs Ag/Ag⁺
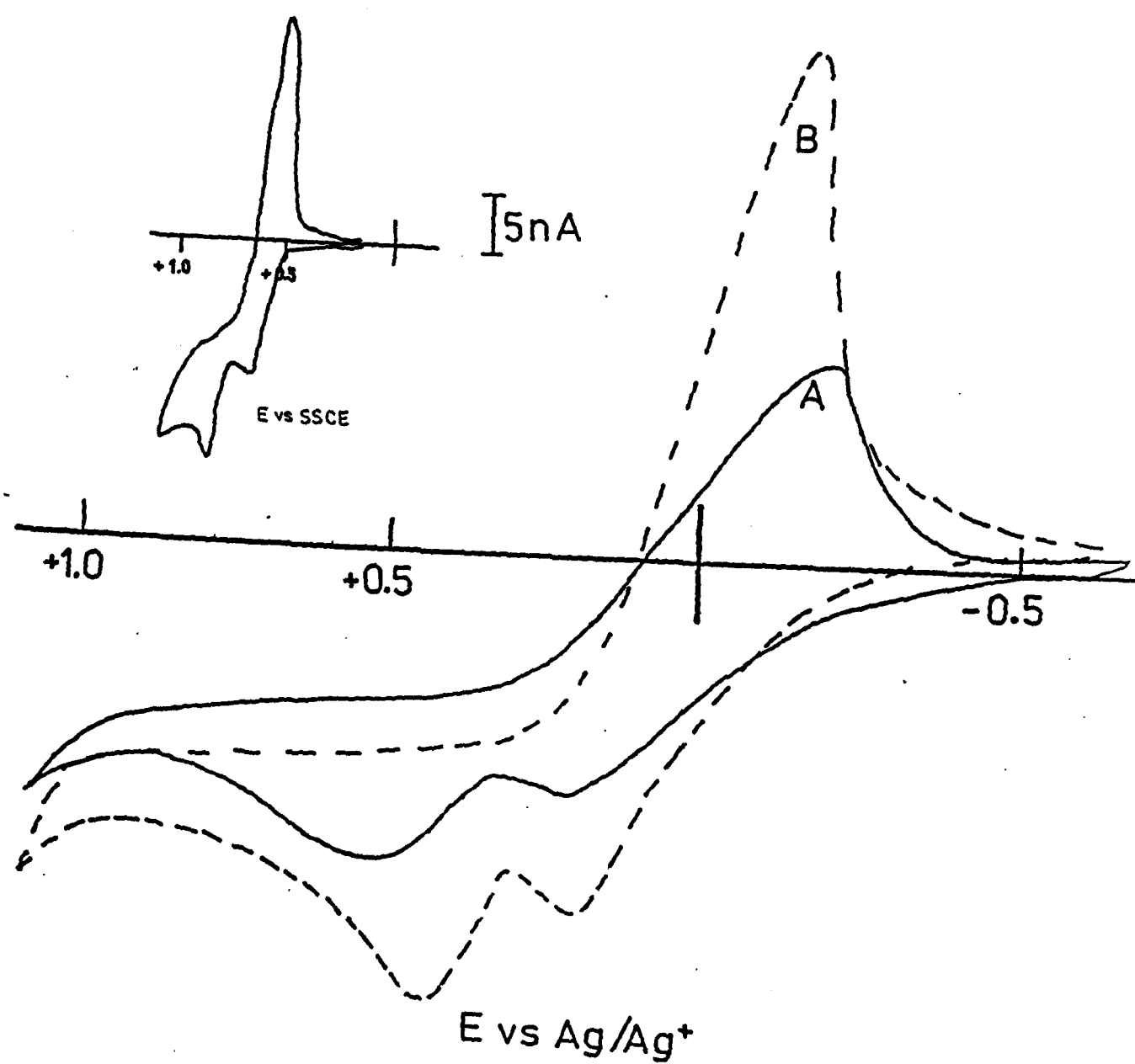
Figure 4

5nA

E vs SSCE

B

A

+1.0   +0.5   -0.5

E vs Ag/Ag⁺
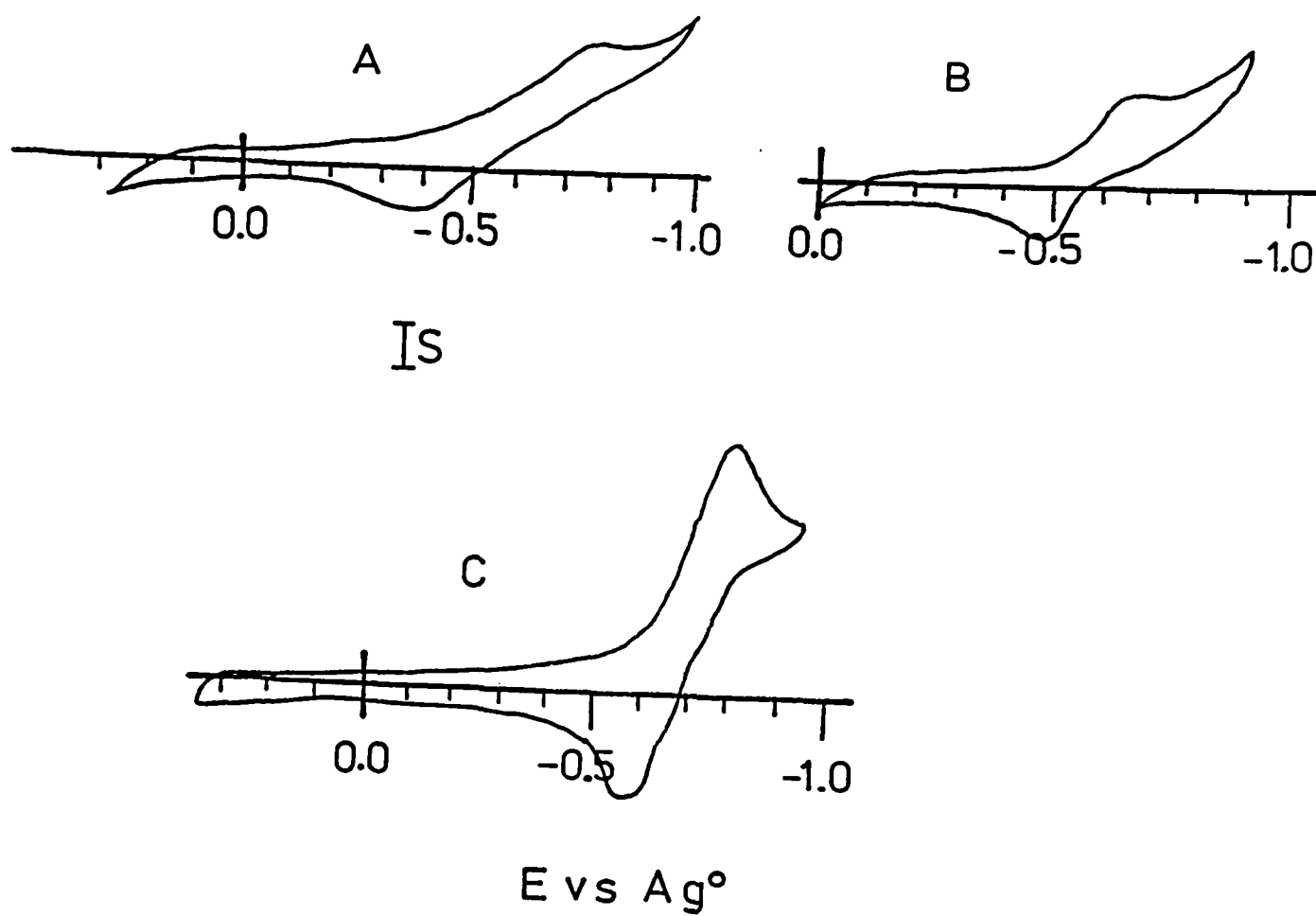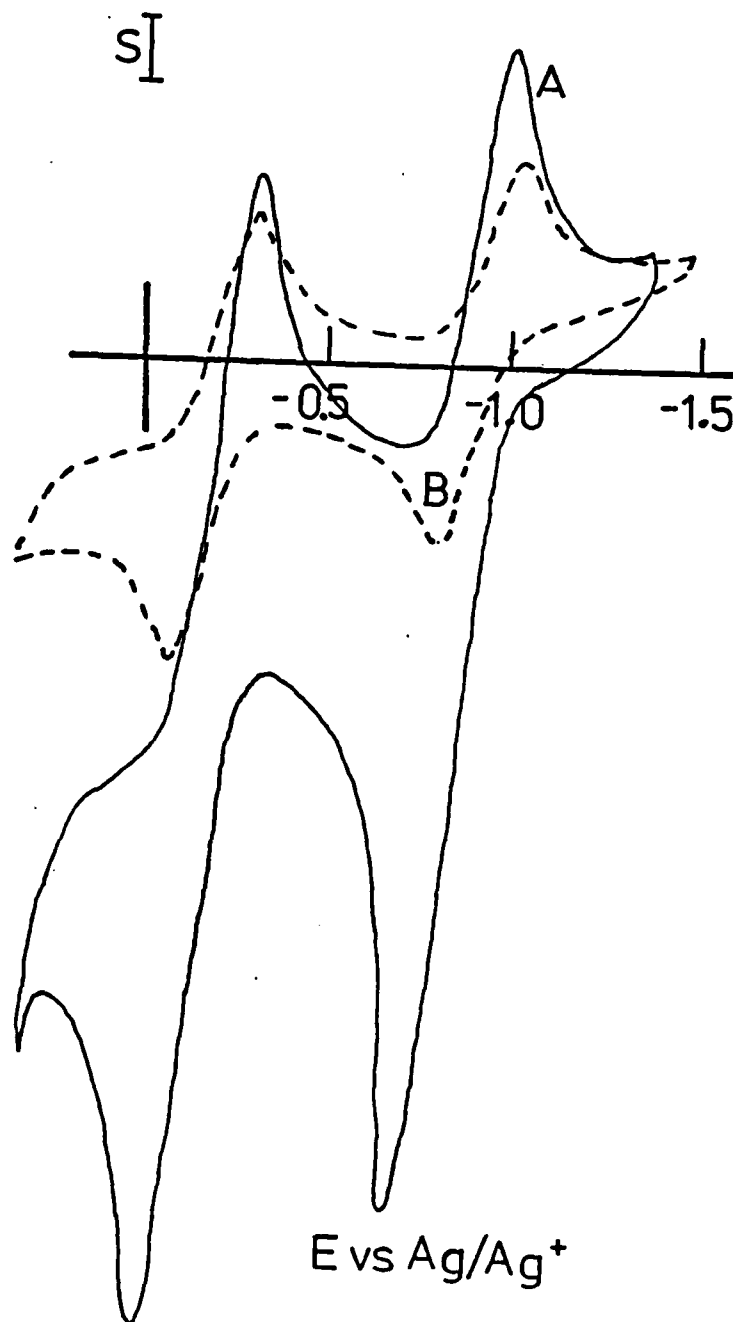
Figure 5

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